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3,256,092 CORROSION INHIBITORS IN BLEACH SOLUTIONS

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This invention relates to novel con-corrosive bleach solutions which are particularly adapted to be used in the field of color photography.

More particularly, this invention relates to stabilized ferricyanide solutions which are employed in color photographic processes to bleach metallic silver to silver salts capable of being removed in subsequent conventional fixing baths.

Alkali ferricyanide bleaching solutions have long been used in color photographic processes for the purpose previously referred to. However, these bleaching solutions suffered from the disadvantages that they had a tendency to corrode the stainless steel containers in which they are usually placed. This corrosion went hand in hand with a decomposition of the bleach solutions. In order to overcome the tendency of these bleaches to corrode stainless steel while being decomposed at the same time, the art resorted to the use of various corrosion inhibitors such as phosphates, nitrates, and dichromates. The inhibitors of the prior art, although fairly effective in preventing degradation of the bleach solutions at a high pH, were not effective at pH ranges of about 4-5 and interfered with the hardening of the photographic emulsion layers to which they were applied. Additionally, it was also quite common for the inhibitors to stain or discolor the emulsion layers. It should be immediately obvious that these side effects of the heretofore employed inhibitors reduced the quality of the final photographic reproductions.

Therefore, it is an object of this invention to provide novel bleach solutions which are stabilized so as to effectively prevent them from corroding stainless steel and from being decomposed and yet are free from ingredients which will impair the quality of the final photographic reproduction.

We have now discovered that the above object can be obtained by employing aliphatic amino polycarboxylic acids and their alkali metal salts such as nitrilotriacetic acid, diethylenetriamine pentaacetic acid, and ethylene diamine tetraacetic acid as corrosion inhibitors for conventional ferricyanide bleach solutions. Other suitable inhibitors include:

1,2-diaminocyclohexane-tetraacetic acid
Hydroxyethylamino-diacetic acid
Dihydroxyethyl-amino-acetic acid
Hydroxyethyl-ethylene-diamino-triacetic acid
Dihydroxyethyldiamine-diacetic acid
Ethylenediamine-di-(ortho-hydroxy-phenylacetic acid)

and various aminopolycarboxylic acids, particularly those shown on pages 88-98 of Robert L. Smith's book, "The Sequestration of Metals," published in 1959 by Chapman & Hall Ltd., London.

All of these compounds have been previously recommended as sequestering agents and water softeners to prevent the precipitation of sludge when using hard water. However, photographic processing solutions are normally prepared from distilled water or at least from very soft water which had been treated with an ion exchange system to decrease its hardness, because even a hardness corresponding to about 43 p.p.m. or even 13 p.p.m., expressed in terms of calcium carbonate, will be objectionable in photographic processes (see page 182 of Eskel

Nordell's book, "Water Treatment," Reinhold Publishing Corporation, New York, N.Y., 1951). The use of these aminopolycarboxylic acids for the prevention of corrosion by ferricyanide solutions, which have a low pH and have been prepared from distilled or very soft water is, therefore, quite unexpected.

The amount of corrosion inhibitor added to conventional ferricyanide bleach solutions is not narrowly critical and can vary over a wide range. However, no particular advantage is gained in corrosion protection when using more than 5 grams of corrosion inhibitor per liter of bleach solution. The preferred concentration is from 1 to 8 grams of inhibitor per liter of bleach solution with 2 to 5 grams per liter being particularly preferred.

The specific ferricyanide bleach solutions to which the inhibitors are added are well known in the art. These bleach solutions are composed of an alkali ferricyanide salt such as potassium ferricyanide and water and may also contain various other ingredients such as alkali metal ferrocyanides, bromides and acetates. It is to be understood that the inhibitors of this invention are effective in all ferricyanide bleaches and are not dependent on any specific formulation.

In more detail, the photographic bleach solutions which are used for the processing of color film contain in aqueous solution an alkali metal ferricyanide such as lithium, potassium or sodium ferricyanide as the oxidizing agent which converts the metallic silver formed during development into a silver salt which is soluble in silver halide solvents such as hypo. Typically, such a bleach solution contains, in addition to the ferricyanide, a halogenizing or converting agent preferably an alkali metal chloride or an alkali metal bromide which converts the silver ferricyanide initially formed in the bleaching reaction into the less soluble silver chloride or silver bromide and thus impels the bleach reaction to completion.

It is essential that the bleach reaction be carried out at a pre-selected pH and consequently, the ferricyanide bleach solutions contain a buffering agent which maintains the desired pH even though small amounts of acids or alkali may be carried into the bleach by the film. The preferred pH of the bleach solutions falls between a range of from 4 to 5. Among the more frequently used ingredients of such buffer mixtures are alkali metal phosphates such as disodium and monosodium phosphate, sodium citrate, sodium bisulfate, citric acid or phthalic acid.

In many instances, other ingredients are added. For example, a metal ferrocyanide is included which gives a tempering action to a freshly mixed bleach solution in order to simulate the performance of a partially used bleach. The rate of bleaching depends on the oxidation reduction potential which in turn is a function of pH and the relative ferrocyanide-ferricyanide concentration. No such oxidation reduction potential can be established so long as ferricyanide only is in the fresh solution, and no ferrocyanide has been formed as a result of the bleaching action. The desired tempering action is achieved by adding to a fresh bleach solution specified amounts of ferrocyanide thus establishing an oxidation reduction potential which otherwise would be set up only after part of the ferricyanide had been reduced to ferrocyanide.

It has also been proposed to prevent the formation of alkali metal ferrocyanide by adding to the fresh bleach solutions an adequate amount of an alkali persulfate such as sodium persulfate, thus keeping the solution continuously oxidized.

The photographic bleach solutions which are contemplated herein contain as their essential ingredients an alkali metal ferricyanide and boric anhydride, together with other bleach adjuvants including buffer mixtures, neutral salts such as sodium sulfate, alkali metal halides,

particularly alkali metal bromides and alkali metal ferrocyanides or alkali metal persulfates. Photographic bleach solutions which we have found stable during storage and processing for considerable periods of time may be compounded in the following proportions, it being understood that all parts are by weight and that sufficient amounts of distilled, soft and preferably demineralized water must be used to make a liter of bleach solution:

	Parts
Alkali metal ferricyanide -----	30 to 120
Alkali metal halide -----	2 to 20
Buffer mixture -----	5 to 30
Alkali metal ferrocyanide -----	2 to 12
or	
Alkali metal persulfate -----	2 to 12
Aminopolycarboxylic acid -----	2 to 5

In compounding the above bleach powder, one may proceed by dissolving first, the alkali metal ferricyanide and adding the other ingredients later. However, if preferred, all the ingredients may be admixed simultaneously. One of the most important advantages of aminopolycarboxylic acid and their salts lies in the fact that its stabilizing and corrosion inhibiting action is most pronounced in an acidic medium, particularly at a pH between 4.0 and 5.0.

The following examples will illustrate the instant invention:

Example I

A bleach solution was prepared by combining the following:

	Grams
Potassium ferricyanide -----	50.0
Potassium ferrocyanide 3H ₂ O -----	5.0
Sodium bromide -----	15.0
Sodium sulfate -----	20.0
Sodium acetate -----	7.5
Ethylene diamine tetraacetic acid -----	5.0
Demineralized water to make 1 liter.	

The above solution had a pH at 20° C. of 4.7 and a high degree of stability. When used in contact with stainless steel processing equipment, the presence of ethylene diamine tetraacetic acid inhibited corrosion effectively, whereas, a type solution without the ethylene diamine tetraacetic acid discolored after short use in stainless steel equipment.

Example II

A solution prepared according to the formulation of Example I with the exception that nitrilotriacetic acid was used instead of ethylene diamine tetraacetic acid. The resulting bleach solution is highly resistive towards corrosion and comparable to the solution of Example I.

Example III

	Grams
Potassium ferricyanide -----	50.0
Potassium ferrocyanide -----	5.0
Sodium bromide -----	15.0
Disodium phosphate -----	11.0
Citric acid -----	8.0
Ethylene diamine tetraacetic acid -----	4.0
Demineralized water to make 1 liter.	

This solution did not deteriorate after 72 hours' storage in a stainless steel container. Under the same testing conditions, an identical solution from which the ethylene diamine tetraacetic acid has been omitted, was badly discolored to a deep blue color during the same period.

Example IV

	Grams
Nitrilotriacetic acid -----	5.0
Potassium ferricyanide -----	30.0
Sodium persulfate -----	4.0
Sodium bromide -----	10.0
Sodium acetate -----	8.0
Citric acid -----	9.0
Disodium phosphate -----	12.0
Demineralized water to make 1 liter.	

This solution was kept for three days at room temperature in a stainless steel container. A solution without nitrilotriacetic acid was badly discolored to a deep blue color under the same testing conditions.

Various modifications such as substituting equivalent materials and varying the proportions of materials used will be obvious to persons skilled in the art. Therefore, the scope of the invention is to be limited solely by the appended claims.

What is claimed is:

1. A photographic bleach solution comprising a solution of an alkali metal ferricyanide and an alkali metal bromide dissolved in demineralized water and having a pH between the range of 4.0 and 5.0, said solution containing as a corrosion inhibitor therefor, an aliphatic compound selected from the group consisting of nitrilotriacetic acid and ethylenediamine tetraacetic acid and the alkali metal salts of said acids, said inhibitor being present in an amount ranging from 1 to 8 grams per liter of bleach solution.

2. A stabilized photographic bleach solution having a pH between the range of 4.0 and 5.0, said solution having the following composition:

	Grams
Alkali metal ferricyanide -----	30 to 120
Alkali metal halide -----	2 to 20
Buffer mixture -----	5 to 30
An aminopolycarboxylic acid compound selected from the group consisting of nitrilotriacetic acid and ethylenediamine tetraacetic acid and the alkali metal salts of said acids -----	1 to 8
Demineralized water to make 1 liter.	

3. A ferricyanide bleach solution according to claim 2 containing as an inhibitor therefor, nitrilotriacetic acid.

4. The composition of claim 3 wherein said nitrilotriacetic acid is present at a concentration of from 2 to 5 grams per liter of solution.

5. A ferricyanide bleach solution according to claim 2 containing as an inhibitor therefor, ethylene diamine tetraacetic acid.

6. The composition of claim 5 wherein the inhibitor is present in a concentration of from 2 to 5 grams per liter of solution.

7. A photographic bleach solution according to claim 2 which contains as an additional ingredient from 2 to 12 grams of an alkali metal ferrocyanide.

8. A photographic bleach solution according to claim 2 which contains as an additional ingredient from 2 to 12 grams of an alkali metal persulfate.

9. A stabilized photographic bleach solution having the following composition:

	Grams
Potassium ferricyanide -----	50.0
Potassium ferrocyanide 3H ₂ O -----	5.0
Sodium bromide -----	15.0
Sodium sulfate -----	20.0
Sodium acetate -----	7.5
Ethylene diamine tetraacetic acid -----	5.0
Demineralized water to make 1 liter.	

10. A stabilized photographic bleach solution having the following composition:

	Grams
Potassium ferricyanide -----	50.0
Potassium ferrocyanide 3H ₂ O -----	5.0
Sodium bromide -----	15.0
Sodium sulfate -----	20.0
Sodium acetate -----	7.5
Nitrilotriacetic acid -----	5.0
Demineralized water to make 1 liter.	

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11. A stabilized photographic bleach solution having the following composition:

	Grams
Potassium ferricyanide	50.0
Potassium ferrocyanide	5.0
Sodium bromide	15.0
Disodium phosphate	11.0
Citric acid	8.0
Ethylene diamine tetraacetic acid	4.0
Demineralized water to make 1 liter.	

12. A stabilized photographic bleach solution having the following composition:

	Grams
Nitrilotriacetic acid	5.0
Potassium ferricyanide	30.0
Sodium persulfate	4.0
Sodium bromide	10.0
Sodium acetate	8.0
Citric acid	9.0
Disodium phosphate	12.0
Demineralized water to make 1 liter.	

13. In a process of inhibiting the corrosive action on stainless steel of an alkali metal ferricyanide bleach solution, said bleach solution having the following composition:

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	Grams
Alkali metal ferricyanide	30 to 120
Alkali metal halide	2 to 20
Buffer mixture	5 to 30
Demineralized water to make 1 liter.	

the improvement, which comprises adding to said solutions as a corrosion inhibitor, from 1 to 8 grams of an aminopolycarboxylic acid compound selected from the group consisting of nitrilotriacetic acid, ethylenediamine tetraacetic acid and the alkali metal salts of said acids.

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